Engineering Tools for designing a metallic removal solution

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Abstract

In this paper, an overview and an analysis is given of the different engineering tools that are at our disposal for designing a metallic removal solution

Introduction

Wet chemistry is the most powerful and the most versatile process available today to remove metallic impurities from surfaces. The state of the elements in the solution is the first important aspect of any wet cleaning chemistry. There are quite a few engineering tools available to predict any contaminants' state in any kind of solution. The next important aspect is the state of the surfaces on wafers. Almost all surfaces of interest can be divided in 2 main groups: the hydroxide terminated oxide or the hydride terminated silicon surface. Both surfaces react very differently with metallic impurities and therefore, the adhesion mechanisms, the adsorption forces and the cleaning solutions should be understood. Different engineering tools exist to approach these questions.

Engineering Tools

The important parameters for cleaning metallic impurities from surfaces are:

- State of the elements in the solution
- State of the surface to be cleaned
- Interactions between the surface and metallic ions

All of the interactions can be understood and modeled by using the following engineering tools:

- Pourbaix diagram
- Standard Reduction Potential Table
- Solubility Product Table
- Reaction constants with silica gel
- Analogy with hydrolysis behavior
- Hydrolysis prediction
- Hydroxides solubility contstants
- Evans diagram
- Chelating agent constants

It is important to understand the usefulness and the information provided by each different engineering tool.
The first engineering tool is the Pourbaix diagram. An example of the Pourbaix diagram for Cu is shown in fig. 1.

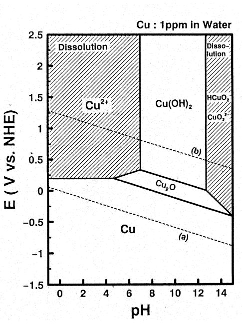

Fig. 1. Pourbaix diagram for Cu.

The Pourbaix diagram is useful in many ways. E.g. in order to review the state of the elements or impurities in solution. The Pourbaix diagram represents the State of the elements a.f.o. pH, redox potential, interacting anions. One has to remark however that it is important to review the interactions that are taken into account when constructing the diagram. The second engineering tool is the standard reduction potential table. This is shown in
table 1.

table 1. Standard reduction potential table.

	E^0 (V vs. NHE)
$O_3 + 2H^+ + 2e^- \Leftrightarrow O_2 + H_2O$	2.07
$H_2O_2 + 2H^+ + 2e^- \Leftrightarrow 2H_2O$	1.776
$Au^{3+} + 3e^- \Leftrightarrow Au$	1.50
$O_2 + 4H^+ + 4e^- \Leftrightarrow 2H_2O$	1.229
$Ag^+ + e^- \Leftrightarrow Ag$	0.799
$Cu^+ + e^- \Leftrightarrow Cu$	0.521
$Cu^{2+} + e^- \Leftrightarrow Cu$	0.337
$2H^+ + 2e^- \Leftrightarrow H_2$	0.000
$Pb^{2+} + 2e^- \Leftrightarrow Pb$	-0.126
$Ni^{2+} + 2e^- \Leftrightarrow Ni$	-0.257
$Fe^{2+} + 2e^- \Leftrightarrow Fe$	-0.440
$SiO_2 + 4H^+ + 4e^- \Leftrightarrow Si + 2H_2O$	-0.857
$A^{3+} + 3e^- \Leftrightarrow Al$	-1.662
$Mg^{2+} + 2e^- \Leftrightarrow Mg$	-2.37
$Na^+ + e^- \Leftrightarrow Na$	-2.714

The disadvantage of this table is that it only provides a 1-dimensional cut of the Pourbaix diagram. The advantage is that more reactions/interactions can be taken into account than in the Pourbaix diagram.
The 3rd engineering tool is the solubility product table shown in table 2 for the hydroxides.

Table 2. Solubility product table for the hydroxides.

Solubility of selected metal hydroxides at pH=7 and pH=10

Metal	*Solubility (ppb) at pH=7*	*Solubility (ppb) at pH=10*
Al^{+++}	$5*10^{-4}$	$5*10^{-13}$
Ca^{++}	Very high	Very high
Cu^{++}	$1*10^{3}$	$1*10^{-3}$
Co^{++}	$6*10^{6}$	6
Fe^{++}	$2*10^{5}$	0.2
Fe^{+++}	$1*10^{-10}$	$1*10^{-19}$
Pb^{++}	300	$3*10^{-4}$
Mg^{++}	Very high	$1*10^{4}$
Mn^{++}	Very high	$1*10^{3}$
Hg^{++}	$6*10^{-4}$	$6*10^{-10}$
Ni^{++}	$3*10^{6}$	3
Sn^{++}	$6*10^{-5}$	$6*10^{-11}$
Zn^{++}	$4*10^{5}$	0.4

The solubility product table of the hydroxides can be used to read out the hydrolysis tendency and therefore the reaction of metallic ions with the silanol groups on the wafer surface. It also shows the precipitation behaviour of metal hydroxides.
Tool nr. 4 are the literature values for silica gel. These constants provide a numerical value to calculate the coverage of the SiO_2 surface with metallic ions.
Tool nr. 5 are the hydrolysis constants. Reaction constants of metallic ions with the silanol surface can be derived from its hydrolysis constant, which can be found in the literature.
Tool nr. 6 is the hydrolysis constant prediction. If the hydrolysis constants are not available or not easily looked up, one can use the charge number and the ionic radius to predict a metals hydrolysis constant.
The hydrolysis constant can also be predicted by using engineering tool nr. 7, which provides us with a prediction based on the hydroxide precipitation table or alternatively the Pourbaix diagram.
The 8th tool available to a cleaning engineer is the Evans diagram. The Evans diagram can be used to calculate the potential of the surface and is important when dealing with bare silicon surfaces. An example of the Evans diagram is shown in fig. 2.

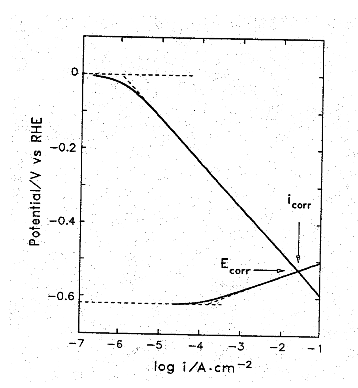

Fig. 2. Evans diagram for Fe in H_2O.

The last tool available is the chelating agent constant tables. These should be used when engineering cleaning solutions with chelating agents.

Summary

In this paper the different engineering tools for approaching metallic impurity interactions with the wafer surface are presented. A thorough understanding of all these tools is fundamental for any cleaning engineer.